

to thermal parameters relative to a , b , c^* . My thanks are due also to Mrs Varwell for help with diagrams; to the Wellcome Trust for a grant for computing and to the University of London Central Research Fund for tape-editing equipment. I must particularly thank Dr R. E. Marsh for most useful suggestions in relation to the orientation of the libration axes.

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A Detailed Refinement of the Crystal Structure of Sodium Tropolonate

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(Received 8 February 1960)

A refinement of the crystal structure of sodium tropolonate, including anisotropic temperature factors, has been carried out using Sasada & Nitta's three-dimensional data. The differential Fourier synthesis and the least-squares methods were used and the two results are compared.

Introduction

The crystal and molecular structure of sodium tropolonate $\text{NaC}_7\text{H}_5\text{O}_2$ was studied by Sasada & Nitta (1956) with three-dimensional line synthesis through atomic centers. The standard deviation of their final bond lengths suggested that more accurate values for the interatomic distances could be obtained by further refinement of their data.

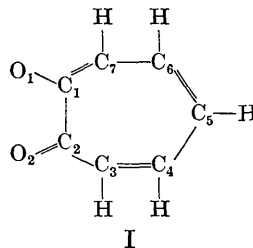
There have been several structure analysis of tropolone derivatives, i.e. cupric tropolone, $\text{C}_{14}\text{H}_{10}\text{CuO}_4$ by Robertson (1951); purpurogallin by Taylor (1952) and by Dunitz (1952); tropolone by Kiruta & Kubo (1953); tropolone hydrochloride, $\text{C}_7\text{H}_7\text{ClO}_2$, by Sasada, Osaki & Nitta (1954) and Sasada & Nitta (1957); tribromo-tropolone, $\text{C}_7\text{H}_3\text{Br}_3\text{O}_2$, by Kubo, Kurita & Kimura (1954); 2-bromo-3-hydroxy-tropone, $\text{C}_7\text{O}_2\text{H}_5\text{Br}$ and 7-bromo-3-hydroxy-tropone by McDonald (1955). All these results except tropolone hydrochloride (1957) were based on one projection of the X-ray data only, or by electron diffraction. Tropolone hydrochloride was refined with three-dimensional data in a similar manner to that of sodium tropolonate.

Since no complete three-dimensional refinement of a structure containing a tropolone ring have been completed we have undertaken this further refinement on the sodium salt using anisotropic temperature factors. A subsidiary purpose of the work was the more complete testing of the differential synthesis and anisotropic structure factor refinement programs which have been written for the IBM 650 computer (Shiono, 1957, 1959).

The numbering of atoms in the tropolonate ion, I,

is the same as used in the earlier paper. The space group of the crystal structure is $P2_1/c$ with 4 molecules in the unit cell,

$$a = 13.91, b = 3.69, c = 11.67 \text{ \AA}, \beta = 93.1^\circ.$$



Three-dimensional refinement by the Fourier method

All the observed data in the Table 2* and Table 3 of the paper by Sasada & Nitta (1956) were used in this refinement. The final coordinates and temperature factors were taken as the starting parameters. Cyclic computations of structure factors followed by the differential synthesis with both observed and calculated structure factors were used to refine the parameters by means of an IBM 650.

The atomic scattering factors for Na, O and C used are those by Berghuis *et al.* (1955). An overall temperature factor of 3.3 \AA^2 was applied in the first calculation of structure factors, and this was changed to 3.2 \AA^2

* All the values in the Table 2 were multiplied by a factor of 2 in order to bring them to the normal scale of the Table 3.

for Na, 3.1 Å² for O₁, O₂, C₁, C₂, C₃ and C₇, 3.2 Å² for C₄, 3.4 Å² for C₅ and C₆ respectively for the second calculation. After the second cycle of refinement, the conventional disagreement index, *R*, reduced from 0.141 to 0.125.

The inspection of the observed and calculated curvatures of atomic peaks at this stage showed the presence of anisotropic thermal motion, therefore, the individual anisotropic temperature factors were introduced for each atom in the further refinement. These temperature factors were determined and refined by the procedure of Cruickshank (1956) and the necessary computations were done by the IBM 650 programs of Shiono (Shiono, 1959, see also Jeffrey & Shiono, 1959*a*).

Two cycles of refinement with anisotropic temperature factors were calculated. The shifts obtained for the temperature parameters were multiplied by a factor of 0.7 before they were applied. As we had

observed in another structure (Jeffrey & Shiono, 1959*a*), a common damping factor seemed to be sufficient for all temperature parameter shifts.

At this stage, the coordinates for hydrogen atoms were evaluated, assuming that they lie in the plane of the adjacent three carbon atoms with a bond distance of 1.07 Å, using an IBM 650 program by Stewart, Lingafelter & Brown (1959). The structure factors were then calculated including those hydrogen atoms with their temperature factors taken as equal to those of their attached carbon atoms. The scattering factor used for hydrogen was that by McWeeny (1951). The disagreement index for this calculation was reduced to 0.098. The calculated structure factors for this last cycle are available on request from the author.

As almost all the shifts of parameters at the end of this cycle were less than half of their standard deviation, the refinement was terminated at this stage.

The final coordinates and temperature coefficients

Table 1. *Final atomic parameters by differential synthesis refinement*

	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>B</i> ₁₁ (Å ²)	<i>B</i> ₂₂ (Å ²)	<i>B</i> ₃₃ (Å ²)	<i>B</i> ₂₃ (Å ²)	<i>B</i> ₃₁ (Å ²)	<i>B</i> ₁₂ (Å ²)
Na	6.5840	1.2028	1.3883	2.78	3.67	2.31	0.15	0.40	0.33
e.s.d.	0.0016	0.0027	0.0018	0.09	0.20	0.10	0.09	0.07	0.09
O ₁	5.4920	-0.7515	0.0777	2.79	4.49	2.53	0.50	0.01	0.05
	0.0028	0.0046	0.0033	0.16	0.40	0.19	0.18	0.14	0.17
O ₂	5.8546	0.5044	-2.2059	2.58	3.89	2.59	0.34	0.44	0.04
	0.0028	0.0045	0.0033	0.16	0.38	0.19	0.17	0.13	0.17
C ₁	4.4423	-0.3899	-0.6061	2.70	2.98	2.08	-0.21	0.29	-0.03
	0.0039	0.0059	0.0044	0.20	0.47	0.23	0.21	0.17	0.21
C ₂	4.6575	0.2954	-1.8927	2.78	2.80	2.18	0.00	-0.01	0.00
	0.0038	0.0057	0.0043	0.20	0.45	0.23	0.21	0.17	0.21
C ₃	3.6039	0.7658	-2.7965	2.77	3.29	2.12	0.10	-0.23	0.37
	0.0043	0.0058	0.0040	0.22	0.51	0.24	0.22	0.18	0.23
C ₄	2.2154	0.7074	-2.7666	2.77	3.65	3.07	-0.09	-0.07	0.39
	0.0044	0.0073	0.0052	0.22	0.51	0.29	0.25	0.19	0.23
C ₅	1.4298	0.1551	-1.7879	2.82	4.42	4.19	-0.93	-0.07	0.09
	0.0043	0.0079	0.0056	0.23	0.59	0.34	0.28	0.22	0.25
C ₆	1.8681	-0.4311	-0.6105	2.93	3.72	3.63	0.05	0.43	-0.29
	0.0044	0.0070	0.0053	0.21	0.56	0.32	0.27	0.21	0.21
C ₇	3.1726	-0.6761	-0.0871	2.76	3.21	2.25	-0.20	0.42	-0.39
	0.0043	0.0055	0.0041	0.21	0.49	0.24	0.22	0.17	0.22

Table 2. *Atomic peak heights, curvatures, by differential synthesis refinement*

		<i>ρ</i>	<i>A</i> _{hh}	<i>A</i> _{kk}	<i>A</i> _{ll}	<i>A</i> _{kl}	<i>A</i> _{lh}	<i>A</i> _{hk}
		Unit: e.Å ⁻³ and e.Å ⁻⁵						
Na	obs.	21.60	-201.12	-154.18	-207.23	-1.01	13.61	7.40
	calc.	21.66	-201.15	-155.42	-207.43	-1.44	13.65	6.74
O ₁	obs.	12.91	-114.92	-89.17	-115.79	3.55	4.73	0.11
	calc.	12.71	-112.97	-88.27	-113.76	3.21	4.63	0.14
O ₂	obs.	13.00	-116.76	-90.87	-115.55	5.10	10.30	0.01
	calc.	12.81	-114.91	-89.81	-114.58	4.60	10.36	-0.10
C ₁	obs.	9.17	-83.35	-69.22	-87.11	-4.71	0.23	-0.91
	calc.	9.33	-84.65	-70.55	-88.68	-4.52	0.68	-0.54
C ₂	obs.	9.50	-87.28	-71.56	-89.83	-5.05	9.79	1.95
	calc.	9.44	-86.69	-71.63	-88.45	-5.02	10.12	1.97
C ₃	obs.	9.12	-75.89	-70.90	-93.92	0.32	4.46	3.95
	calc.	9.31	-78.20	-72.03	-94.62	0.10	4.31	2.20
C ₄	obs.	8.24	-74.20	-55.99	-73.30	-3.09	0.43	5.03
	calc.	8.34	-74.88	-56.94	-73.86	-3.24	0.86	4.75
C ₅	obs.	8.03	-76.07	-51.66	-68.19	-5.11	1.36	4.86
	calc.	7.78	-73.26	-50.48	-66.48	-4.61	1.70	2.78
C ₆	obs.	8.23	-74.13	-58.67	-71.31	-7.01	8.37	-0.31
	calc.	8.17	-73.55	-58.36	-70.81	-6.99	7.66	0.31
C ₇	obs.	9.22	-76.71	-73.81	-91.59	-5.86	7.69	-0.23
	calc.	9.21	-76.55	-73.17	-90.95	-5.22	7.55	-0.16

Table 3. *Final atomic parameters by least-squares refinement*

	X (Å)	Y (Å)	Z (Å)	B ₁₁ (Å ²)	B ₂₂ (Å ²)	B ₃₃ (Å ²)	B ₂₃ (Å ²)	B ₃₁ (Å ²)	B ₁₂ (Å ²)
Na	6.5836	1.2041	1.3872	3.068	4.029	2.563	0.109	0.370	0.399
	0.0020	0.0031	0.0019	0.102	0.154	0.097	0.085	0.069	0.087
O ₁	5.4981	-0.7565	0.0802	2.826	4.580	3.078	0.607	-0.016	-0.026
	0.0037	0.0054	0.0040	0.152	0.253	0.151	0.174	0.113	0.164
O ₂	5.8560	0.4979	-2.2078	2.834	3.865	2.824	0.462	0.759	-0.007
	0.0036	0.0051	0.0036	0.147	0.225	0.144	0.164	0.111	0.151
C ₁	4.4292	-0.3967	-0.6073	3.009	3.711	2.570	-0.241	-0.170	-0.059
	0.0050	0.0076	0.0048	0.201	0.302	0.184	0.221	0.150	0.214
C ₂	4.6500	0.2999	-1.8937	2.852	3.107	2.468	-0.286	0.154	-0.149
	0.0049	0.0071	0.0048	0.189	0.274	0.175	0.197	0.137	0.194
C ₃	3.5951	0.7680	-2.7974	3.197	3.610	2.377	0.248	-0.117	0.305
	0.0056	0.0070	0.0051	0.203	0.296	0.169	0.205	0.147	0.223
C ₄	2.2206	0.7010	2.7703	3.201	4.306	2.939	-0.008	-0.159	0.480
	0.0057	0.0079	0.0054	0.207	0.343	0.194	0.248	0.159	0.242
C ₅	1.4333	0.1646	-1.7886	2.753	4.264	4.222	-1.132	-0.293	0.291
	0.0054	0.0083	0.0061	0.198	0.365	0.251	0.275	0.176	0.247
C ₆	1.8752	-0.4462	-0.5994	2.881	4.245	3.953	-0.365	0.558	-0.457
	0.0055	0.0082	0.0061	0.204	0.345	0.237	0.272	0.172	0.224
C ₇	3.1712	-0.6815	-0.0882	3.235	3.167	2.398	-0.182	0.546	-0.376
	0.0051	0.0069	0.0051	0.215	0.383	0.167	0.210	0.151	0.206

Table 4. *Distances to the best plane C₁ ~ C₇*

	Diff. synthesis refinement	Least-squares refinement
C ₁	-0.007 ₄ Å	-0.009 ₈ Å
C ₂	-0.005 ₉	-0.001 ₄
C ₃	0.010 ₇	0.011 ₃
C ₄	0.001 ₈	-0.006 ₄
C ₅	-0.013 ₆	-0.004 ₅
C ₆	0.006 ₅	0.003 ₃
C ₇	0.007 ₈	0.007 ₄
O ₁	-0.030 ₉	-0.028 ₃
O ₂	0.006 ₉	0.001 ₁

Equation of the plane

DS -0.0291X + 1.2413Y + 0.6540Z + 1 = 0

LS -0.0292X + 1.2314Y + 0.6518Z + 1 = 0

for the Fourier refinement with their standard deviation (Cruickshank, 1949, 1950, 1954, 1956) are given in Table 1. The observed and calculated peak heights and their derivatives are listed in Table 2.

The equation of the best fit plane for the seven carbon atoms was calculated by least squares using the 650 program by Stewart (1959) and is given as

$$-0.291X + 1.2413Y + 0.6540Z + 1 = 0.$$

The distance to the plane from each atom are listed in Table 4. The electron densities at the assumed hydrogen positions were calculated by difference differential synthesis method and they are 1.17 e.Å⁻³ for H(C₃) and H(C₄), 0.88 for H(C₅), 1.16 for H(C₆) and 1.02 for H(C₇), respectively.

Refinement by least-squares method

The full matrix least-squares refinement program with anisotropic temperature factors for IBM 704 computer by Busing & Levy (1959) was used. Since we had observed elsewhere certain differences in results of refinements between Fourier and least-squares methods with isotropic temperature factors (Jeffrey & Shiono,

1959a), the structure was refined by this least-squares program for the purpose of comparison.

Table 5. *Interatomic distances*

	Diff. synthesis	Least squares	e.s.d. (DS)
Na-O ₁	2.402 Å	2.393 Å	0.004 Å
	2.450	2.447	
	2.564	2.564	
Na-O ₂	2.370	2.367	0.004
	2.398	2.397	
	2.576	2.580	
O ₁ -C ₁	1.274	1.290	0.005
O ₂ -C ₂	1.271	1.278	0.005
C ₁ -C ₂	1.484	1.490	0.006
C ₂ -C ₃	1.430	1.430	0.006
C ₁ -C ₇	1.426	1.416	0.006
C ₃ -C ₄	1.392	1.378	0.006
C ₇ -C ₆	1.401	1.387	0.006
C ₄ -C ₅	1.401	1.398	0.007
C ₆ -C ₅	1.366	1.388	0.007

Table 6. *Bond angles*

	Diff. synthesis	Least squares	e.s.d. (DS)
∠ O ₁ C ₁ C ₂	116.3	115.7	0.4°
∠ O ₂ C ₂ C ₁	118.2	118.1	0.4
∠ O ₁ C ₁ C ₇	118.2	118.4	0.4
∠ O ₂ C ₂ C ₃	117.5	117.9	0.4
∠ C ₁ C ₂ C ₃	124.3	124.1	0.4
∠ C ₂ C ₁ C ₇	125.6	125.9	0.4
∠ C ₂ C ₃ C ₄	132.4	132.4	0.4
∠ C ₁ C ₇ C ₆	131.2	131.4	0.4
∠ C ₃ C ₄ C ₅	129.0	129.2	0.4
∠ C ₅ C ₆ C ₇	130.2	130.0	0.5
∠ C ₄ C ₅ C ₆	127.3	127.2	0.5

The final positional and temperature parameters from the differential Fourier synthesis refinement were used as the starting parameters in the least-squares cycle. The function minimized is $\sum w(F_o - F_c)^2$ and the weighting scheme of Hughes (1941) was used with zero weights for unobserved reflections. All

Table 7. Comparison of the final parameters by differential synthesis and least-squares refinement

	Mean differences in atomic coordinates			Mean differences in thermal parameters		
	Δ	e.s.d. (DS)	e.s.d. (LS)	Δ	e.s.d. (DS)	e.s.d. (LS)
Na	0.0009 Å	0.002 Å	0.002 Å	0.173 Å ²	0.11 Å ²	0.10 Å ²
O ₁	0.0045	0.004	0.004	0.149	0.21	0.17
O ₂	0.0033	0.004	0.004	0.174	0.20	0.16
C ₁	0.0070	0.005	0.006	0.341	0.25	0.21
C ₂	0.0043	0.005	0.006	0.211	0.25	0.19
C ₃	0.0040	0.005	0.006	0.222	0.27	0.21
C ₄	0.0050	0.006	0.006	0.247	0.28	0.22
C ₅	0.0045	0.006	0.007	0.142	0.32	0.25
C ₆	0.0111	0.006	0.007	0.267	0.30	0.24
C ₇	0.0026	0.005	0.006	0.137	0.26	0.21

hydrogen atoms were included with assumed positions in the calculation but their parameters were not refined.

After three cycles of refinement, the largest shift of parameters was less than one tenth of its standard deviation. The final parameters with their standard deviations are given in Table 3, bond lengths and angles are given in Tables 5 and 6. The 'best-fit' plane through seven carbon atoms and the distances from each atom to the plane are given in Table 4. The final disagreement factor R was 0.110.

Comparison of the two refinement results

The average differences in atomic coordinates and temperature factors with their estimated standard deviation by both methods are given in Table 7. Inspection of the table shows that for 56 out of the 90 parameters the difference is less than its estimated standard deviation. The distribution of differences in positional and thermal parameters in regard to their estimated standard deviations are given in Table 8.

Table 8. Distribution of differences in parameter (DS versus LS)

Difference standard deviation	Number of parameters (positional, thermal)	%
0 ~ 0.50	30 (10, 20)	0.333
0.51 ~ 1.00	26 (11, 15)	0.289
1.01 ~ 1.50	10 (3, 7)	0.111
1.51 ~ 2.00	12 (5, 7)	0.133
2.01 ~ 2.50	5 (0, 5)	0.056
2.51 ~ 3.00	5 (1, 4)	0.056
3.01 ~ 3.50	1 (0, 1)	0.011
3.51 ~ 4.00	1 (0, 1)	0.011

There is no apparent systematic tendency in the differences of positional and thermal parameters by the two methods. This is in good agreement with our previous experience in a non-centrosymmetric structure (Jeffrey & Shiono, 1959*b*). The slightly larger differences in temperature parameters may be due to the fact that the least-squares program used only thirteen entries for an atomic scattering factor table with Cu $K\alpha$, so that interpolation errors could affect the temperature parameters.

Discussion of the structure

Although the previous analysis (Sasada & Nitta, 1956) had suggested some asymmetry, it is reasonable to expect that, in the absence of distorting interionic forces, the tropolonate ion would have C_{2v} symmetry due to the degeneracy of the resonance structure. The comparison of the corresponding bond lengths in Table 5 showed that all corresponding bonds are equal in terms of their estimated standard deviations from both refinement techniques, except the bonds C₄-C₅, C₆-C₅ from the result of the differential synthesis. However, the coordinate standard deviation from the Fourier synthesis given by the Cruickshank method can be underestimated by as much as 50% in some cases (Broadley *et al.*, 1959), due to the effect of accidentally absent planes; in this analysis there were 386 unobserved reflections out of ca. 1240 within the reflecting limit. If allowance is made for this underestimate, then both results confirms the C_{2v} symmetry within the estimated standard deviations of coordinates. The bond lengths from the two refinements are shown in Fig. 1.

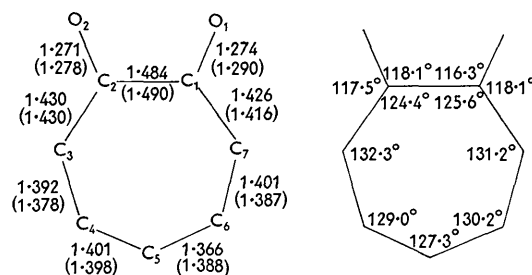


Fig. 1. Bond lengths and angles. Those by differential synthesis are shown without brackets. Numbers in brackets are by least squares.

Combining the results of the two refinement techniques with equal weight and averaging the symmetry related bonds, the following bond lengths and angles given in Table 9 were obtained. We believe these to represent the best data on the tropolonate ion at present available.

Cruickshank (1956*b*) has shown that systematic errors in atomic positions may arise from rotational oscillations of molecule, the atoms appearing closer to

Table 9. Mean bond lengths and angles

O ₁ -C ₁ (O ₂ -C ₂)	1.278 Å
C ₁ -C ₂	1.487
C ₂ -C ₃ (C ₁ -C ₇)	1.426
C ₃ -C ₄ (C ₇ -C ₆)	1.390
C ₄ -C ₅ (C ₆ -C ₅)	1.388
∠ O ₁ C ₁ C ₂ (∠ O ₂ C ₂ C ₁)	117.1°
∠ O ₁ C ₁ C ₇ (∠ O ₂ C ₂ C ₃)	118.0
∠ C ₁ C ₂ C ₃ (∠ C ₂ C ₁ C ₇)	125.0
∠ C ₂ C ₃ C ₄ (∠ C ₁ C ₇ C ₆)	131.9
∠ C ₃ C ₄ C ₅ (∠ C ₇ C ₆ C ₅)	129.6
∠ C ₄ C ₅ C ₆	127.3

the molecular mass center than their real positions. No detailed analysis of translational and rotational oscillations of molecules has been attempted in this crystal, but from comparisons of temperature factors with other completely analyzed structures by Cruickshank (i.e., anthracene, 1956; naphthalene, 1957) the correction to the bond lengths would likely be the order of 0.005 Å in the sense of making bond lengths longer.

For the planarity of the molecule, all seven carbon atoms and an oxygen (O₂) atom lie in a plane within 0.014 Å and O₁ is 0.03 Å off this plane. All the deviations from the plane are not significant in terms of their standard deviation along *y* direction except that of O₁. A sodium atom is surrounded by six oxygen atoms of distance ranging 2.37 to 2.58 Å, and an oxygen atom is in turn surrounded by three sodium atoms. An asymmetric distribution of the ionic forces may possibly be responsible for the small out-of-plane deviation of O₁.

Table 10. Distance of non-bonded atoms

		Differential synthesis	
Na	Na	3.18 ₃ Å	(1-x, 1-y, -z)
	C ₁	3.13 ₆	(1-x, -y, -z)
	C ₂	3.07 ₈	(1-x, -y, -z)
O ₁	O ₂	3.25 ₁	(1-x, -y, -z)
	O ₁	3.30 ₀	(1-x, 1-y, -z)
O ₂	O ₂	3.25 ₇	(1-x, -½+y, ½-z)
C ₁	C ₂	3.28 ₀	(x, 1+y, z)
	C ₃	3.42 ₄	(x, 1+y, z)
C ₂	C ₃	3.49 ₁	(x, 1+y, z)
	C ₇	3.56 ₄	(x, 1+y, z)
C ₃	C ₄	3.39 ₂	(x, 1+y, z)
	C ₆	3.37 ₁	(x, 1+y, z)
C ₄	C ₅	3.34 ₀	(x, 1+y, z)
	C ₆	3.34 ₀	(x, 1+y, z)

Almost all the short distances of non-bonded atoms occur along *y* direction between two molecules in the neighboring units cells. Those distances are listed in Table 10.

Using the Pauling's equation (1952) and the resonance formulae given in Sasada & Nitta's paper (1956, Fig. 7), it is no longer necessary to assume any asymmetry in the resonance states in order to calculate the bond lengths which are consistent with the results of the present work. The best calculated bond lengths, which are not significantly different from the observed

values using the statistical criteria of Cruickshank & Robertson (1953), were obtained by taking the following weights:

I-II, 25%; III-IV, 7%; V-VI, 5%; VII-VIII, 3%; IX, 2%; X-XI, 7%; XII, 4%

and the calculated values are C-O 1.27, C₁-C₂ 1.48, C₂-C₃ 1.41, C₃-C₄ 1.39 and C₄-C₅ 1.40 in Å.

When the results in Table 9 are compared with the results of the molecular orbital calculation (Kurita & Kubo, 1951), there is no significant difference between the two values of the C-O bond and three of the C-C bonds; however, in the bond C₁-C₂, the difference of 0.047 Å is highly significant in terms of the deviation.

From the bond lengths of tropolone hydrochloride (Sasada & Nitta, 1957), the average bond lengths of related bonds with C_{2v} are: C-O 1.36 Å; C₁-C₂ 1.39 Å; C₂-C₃ 1.41 Å; C₃-C₄ 1.40 Å; C₄-C₅ 1.40 Å.

When these are compared with the present results, all carbon-carbon bonds agree within the standard deviation of the former results, except C₁-C₂ which is considerably shorter in the hydrochloride. This could be explained by the consideration of the resonance formulae (Fig. 6 of Sasada & Nitta, 1957) whereby the types V, VI and IX account for about 50%. However, this observation requires verification by an anisotropic refinement similar to that described here. The C-O bonds in the cation are, as would be expected, longer than those in the anion.

The author wishes to thank Prof. I. Nitta and Dr Y. Sasada for the use of their data, Prof. G. A. Jeffrey for valuable discussions and Dr W. R. Busing for supplying us with the least-squares program.

This research was supported by a grant from The National Science Foundation.

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Interpretation of Diffractometer Line Profiles Distortion due to the Diffraction Process*

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(Received 24 December 1959 and in revised form 13 January 1960)

On the basis of the kinematic theory of powder diffraction it is shown that the angle factor

$$J(\theta) \propto \sin^2 \theta \cos \theta / (1 + \cos^2 2\theta)$$

describes the distortion of the line profile due to the diffraction process when the incident radiation consists of a spectral distribution $h_1(\lambda)$ (the angle scale equivalent of which is $h(\epsilon)$). The distortion includes the effects of the Lorentz and polarization factors, trigonometric factors associated with the experimental powder method and the effects of physical absorption.

In the absence of other aberrations the angle scale spectral distribution $h(\epsilon)$ is (to the first order) recovered from the observed distribution $f(\epsilon)$ from the equation

$$f(\epsilon)J(\theta) = h(\epsilon).$$

A_{LPU} the correction to be applied to counterbalance the shift in the observed profile due to the distortion of the profile caused by the diffraction process, is inferred from $J(\theta)$ and is applicable to crystal powders encountered in precision lattice parameter determinations.

1. Introduction

In three earlier papers (Ladell, Parrish & Taylor, 1959*a, b*; Ladell, Mack, Parrish & Taylor, 1959; hereinafter abbreviated as *LPTa, b*, *LMPT*), the interpretation of diffractometer line profiles by the method of centroids was discussed. In these papers attention was primarily focussed on operational procedures required in precision lattice parameter determinations. It was shown that it was necessary to correct the centroids of observed profiles for the effect of dispersion and the distortion due to the angle factor (Lorentz, polarization and geometric powder factors) which arises from the diffraction process.

In this paper the role of the diffraction process in the generation of diffractometer line profiles of polycrystalline specimens will be considered in greater detail. Using less restrictive assumptions than those which were used in the classical derivation of the integrated intensity formula for powder diffraction, it will be shown that the angle factor

$$J(\theta) \propto \sin^2 \theta \cos \theta / (1 + \cos^2 2\theta) \quad (1)$$

arises inherently from the diffraction process (when absorption is included) and describes the distortion of the angle scale spectral distribution in the absence of other aberrations.

In an earlier treatment Pike (1959) considered the effects of the Lorentz and polarization factors for two extreme limiting cases, but did not consider the effect of absorption. In an accompanying note (Pike & Ladell,

* This research was partially supported by the United States Air Force through the Air Force Office of Scientific Research (ARDC).